



Short communication

Powering microbial electrolysis cells by capacitor circuits charged using microbial fuel cell

Marta C. Hatzell^a, Younggy Kim^{b,1}, Bruce E. Logan^{b,*}^a Department of Mechanical and Nuclear Engineering, The Pennsylvania State University, University Park, PA 16802, USA^b Department of Civil and Environmental Engineering, 131 Sackett Building, The Pennsylvania State University, University Park, PA 16802, USA

H I G H L I G H T S

- MFC–MEC coupled systems enhanced with parallel aligned MFCs and capacitor circuit.
- Hydrogen production rates and energy recoveries increased by as much as 212% and 77%.
- Capacitor energy storage based circuit transferred charge with 90% efficiency.

A R T I C L E I N F O

Article history:

Received 21 August 2012

Received in revised form

29 November 2012

Accepted 1 December 2012

Available online 12 December 2012

Keywords:

Microbial fuel cell

Microbial electrolysis cell

Capacitor

Energy recovery

Voltage reversal

A B S T R A C T

A microbial electrolysis cell (MEC) was powered by a capacitor based energy storage circuit using energy from a microbial fuel cell (MFC) to increase MEC hydrogen production rates compared to that possible by the MFC alone. To prevent voltage reversal, MFCs charged the capacitors in a parallel configuration, and then the capacitors were discharged in series to boost the voltage that was used to power the MECs. The optimal capacitance for charging was found to be ~ 0.01 F for each MFC. The use of the capacitor charging system increased energy recoveries from 9 to 13%, and hydrogen production rates increased from 0.31 to 0.72 $\text{m}^3 \text{m}^{-3}\text{-day}^{-1}$, compared to coupled systems without capacitors. The circuit efficiency (the ratio of the energy that was discharged to the MEC to the energy provided to the capacitor from the MFCs) was $\sim 90\%$. These results provide an improved method for linking MFCs to MECs for renewable hydrogen gas production.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

Microbial electrolysis cells (MECs) represent a promising method for using bacteria to convert organic waste into electrical current to electrochemically produce hydrogen [1–4]. Due to the voltage produced by bacteria on the anode, hydrogen gas can be evolved at the cathode by additionally applying more than ~ 0.2 V [1,2], with typical applied voltages >0.5 V [3,4]. This applied voltage is much less than that needed for water electrolysis (>1.2 V), but an additional goal to make this process truly green and sustainable is to remove the need for electrical grid energy. Large scale realization of a green MEC technology is currently contingent on the input electricity coming from renewables such as solar, wind, or salinity

gradient energy [5,6]. Another practical electrical energy source is a microbial fuel cell (MFC). MFCs use bacteria to generate electricity from the oxidation of organic matter and the reduction of oxygen. This electricity produced by the MFC can be used to power an MEC, thus avoiding the need for electrical grid energy. Coupled together, the dual bioelectrochemical system (BES) has the advantage of removing organics from wastewater while generating hydrogen, without consuming any electrical grid energy.

The use of MFCs to directly power MECs has been previously proposed [7–11], but the performance of these systems has been limited by low voltages produced when the two systems were directly connected. Sun et al. [7] combined a single two-chamber MEC (450 mL) to an MFC (225 mL), and achieved a maximum hydrogen production rate of 0.0149 $\text{m}^3 \text{H}_2 \text{m}^{-3} \text{day}^{-1}$. This hydrogen production rate was significantly less than reported values obtained using a power supply at $E_{\text{ap}} = 0.8$ V (>4 $\text{m}^3 \text{H}_2 \text{m}^{-3} \text{day}^{-1}$) [12]. Furthermore, the coupled system was unstable, and small reductions in MFC or MEC voltage substantially reduced hydrogen gas production. To improve the performance (voltage),

* Corresponding author. Tel.: +1 814 863 7908; fax: +1 814 863 7304.

E-mail address: blogan@psu.edu (B.E. Logan).¹ Present address: Department of Civil Engineering, McMaster University, Hamilton, ON L8S 4L7, Canada.

multiple MFCs connected in series and in parallel were used as the power source [8]. With three MFCs (350 mL each) connected in series to a two chamber MEC, hydrogen production rates still did not improve ($0.0145 \text{ m}^3 \text{ H}_2 \text{ m}^{-3} \text{ day}^{-1}$) even though applied voltages increased to 0.807 V. Parallel connection of three MFCs to power the MEC resulted in a hydrogen production rate of only $0.00750 \text{ m}^3 \text{ H}_2 \text{ m}^{-3} \text{ day}^{-1}$. Performance of coupled systems were improved by varying the size of the MFCs relative to the MECs [9]. Wang et al. [9] used one to three MFCs (each 25 mL) connected in series to power a single 25 mL or 75 mL MEC. Multiple MFCs in series did not improve the performance relative to a single MFC, but the maximum hydrogen production rate with the single chamber MEC was significantly improved with the larger (75 mL) MEC ($0.48 \text{ m}^3 \text{ H}_2 \text{ m}^{-3} \text{ day}^{-1}$). The use of the larger MEC increased the MFC voltage and therefore achieved higher hydrogen production rates. The increase was possibly due to the increased internal resistance of the MEC which resulted in the MECs operating at higher potentials. The use of multiple MFCs connected in series is also not feasible over an extended period of time due to voltage reversal, where the polarity of the anode or cathode switches. Voltage reversal reduces the voltage produced by the MFCs, and causes irreversible damage to the bioanode [13,14].

Several approaches have been used to increase voltage production by MFCs. One approach is to use power management systems to boost MFC voltages through the use of charge-pumps [15–17], diodes [18], DC/DC converters [15], batteries [19], and capacitors [15,19,20]. Others have focused on optimizing system operation, through maximum power point tracking (MPPT) to enhance the total energy extracted and system efficiency [17,21–24]. While performance improvements have been demonstrated in terms of voltage production, many of the boosting systems have poor circuit efficiencies. One of the more promising method for producing higher voltages is the use of capacitor circuits [17,20]. A capacitor based circuit was examined here as a method to efficiently transfer energy and boost applied voltages from MFCs to MECs. In this approach, multiple MFCs are used to charge capacitors in parallel, and then the charged capacitors are discharged in series, improving voltage production and hydrogen energy recoveries. This approach avoids the use of energy consuming diodes, which typically produce voltage drops on the order of $\sim 0.25 \text{ V}$ (Schottky Diode) and $\sim 0.7 \text{ V}$ (traditional Diode), allowed for high circuit efficiencies and optimal system recovery [25]. The ideal capacitance per MFC, and the number of MFCs used in parallel were examined to optimize system stability and performance.

2. Materials and methods

2.1. Reactor preparation and set up

Cube-shaped, single-chamber MFC and MEC reactors were constructed from a solid block of Lexan to produce a 28 mL cylindrical chamber [26]. A glass tube (8 cm length, 1.6 cm diameter) was attached to the top of the MEC to collect hydrogen gas [3]. Brush anodes 27 mm in diameter and 23 mm in length (Mill Rose Lab Inc., OH) were made from graphite fibers and a titanium wire core [27]. MFC cathodes were made from wet-proofed (30%) carbon cloth (7 cm^2) and contained a Pt catalyst (0.5 mg cm^{-2}) on the water facing side, and 4 PTFE diffusion layers on the opposite side [28]. MEC cathodes were made from type 304 stainless steel, and contained a Pt loading (0.5 mg cm^{-2}) with no diffusion layers.

All anodes were initially started up in MFCs that were inoculated with effluent from an operating MFC (50%), and 50 mM PBS buffer (32.3 mM Na_2HPO_4 , 17.8 mM $\text{NaH}_2\text{PO}_4\text{--H}_2\text{O}$; 5.8 mM NH_4Cl ; 1.7 mM KCl; conductivity 7.4 mS cm^{-2} , pH = 7), 12.2 mM sodium acetate, and a trace nutrient solution [29]. Once the MFCs reached

reproducible maximum voltages over three consecutive fed batch cycles, the anode was assumed to be fully acclimated. Following this startup period, some of the anodes were transferred into MECs. At the start of each feeding cycle, the anode solutions of the MECs were sparged with N_2 gas to remove dissolved oxygen [3].

2.2. Capacitor circuit

A capacitor-based circuit was used to boost the voltage, obtained from various numbers of MFCs aligned in parallel, which was applied to a single MEC. The circuit was made up of 0.01 F capacitors (RadioShack, TX) and DPDT relays (5V/2A MT2, AXICOM, Wilmington, DE), which were controlled by a programmable microcontroller (MEGA 2560, Arduino, Italy). The 0.01 F capacitor was chosen because it could rapidly charge and discharge. The MFCs charged the capacitors in parallel, and then the capacitors were discharged in series as the power source for the MEC (Fig. 1). Two arrays of capacitors were used so that one array of capacitors was being charged by the MFCs, while the other array was delivering charge to the MEC. The number of capacitors in each array was varied in order to investigate the effect of total capacitance on system performance, and the number of MFCs used was varied to examine the effect of total applied energy.

2.3. Experiments and measurements

During testing the voltage across the MFCs, MEC and a 10Ω resistor (used to calculate current) was continuously monitored every 20 min using a digital multi-meter (model 2700, Kiethley Instruments, Inc., OH). Volumetric gas production was monitored using a respirometer (AER-200; Challenge Environmental, AR), and the gas was collected in a gas bag for further analysis (0.1 L capacity; Cali-5 Bond, Calibrated Instruments, NY). Gas samples were analyzed for H_2 , N_2 , and CH_4 using a gas chromatograph (GC, model 310 SRI Instruments argon carrier gas, CA). After each fed batch cycle, the change in chemical oxygen demand (COD) was measured according to standard methods (Hach Co., CO).

2.4. Calculations

MFC performance was determined by quantifying the amount of coulombs produced from the substrate utilized, known as coulombic efficiency, using

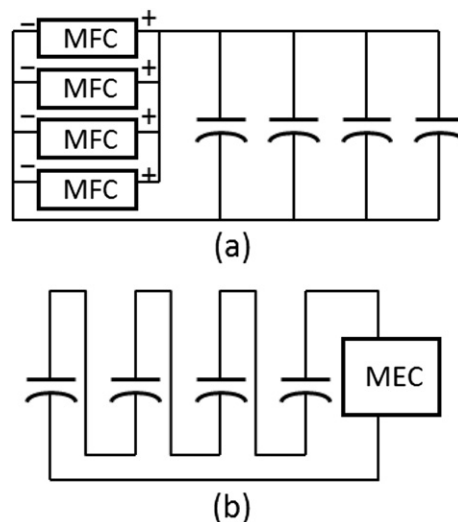


Fig. 1. Capacitor based circuit (a) charging capacitors in parallel (b) discharging capacitors in series.

$$CE_{MFC} = \frac{8 \int i dt}{FV\Delta COD} \quad (1)$$

where i is the current generated from the total MFCs in parallel, F is Faradays constant, V is the total MFC anode volume, and ΔCOD is the change in COD over the fed batch cycle. MEC performance was evaluated in terms of the hydrogen production rate Q ($\text{m}^3 \text{H}_2 \text{m}^{-3} \text{d}^{-1}$), and hydrogen yield, Y_{MEC} ($\text{mol H}_2 \text{mol COD}^{-1}$), as previously described [3].

The entire system performance was evaluated in terms of overall hydrogen yield (Y_{SYS}), COD removal, coulombic efficiency (CE_{SYS}), and energy recovery (r_E) using

$$Y_{SYS} = \frac{n_{H_2}}{V_{total}(\Delta COD_{MFC} + \Delta COD_{MEC})} \quad (2)$$

$$CE_{SYS} = \frac{8 \int i dt}{FV_{total}(\Delta COD_{MEC} + \Delta COD_{MFC})} \quad (3)$$

$$r_E = \frac{n_{H_2} \Delta H_{H_2}}{n_{s,MFC} \Delta H_s + n_{s,MEC} \Delta H_s} \quad (4)$$

where n_{H_2} is the moles of hydrogen collected, ΔCOD_{MEC} and ΔCOD_{MFC} are the changes in COD over each test for the MFCs and MECs, $n_{s,MFC}$ and $n_{s,MEC}$ are the number of moles of substrate consumed in the MFCs and MECs, ΔH_{H_2} and ΔH_s are the heats of combustion for either the product (hydrogen) or substrate (acetate) in kJ mol^{-1} , and V_{total} is the liquid volume in both the MFCs and MEC.

3. Results and discussion

3.1. Voltages produced by MFCs using the capacitor circuit

When multiple MFCs were connected in parallel (2M, 3M or 4M), the maximum voltage produced was ~ 0.3 V. When a two capacitor circuit was connected to the MFCs in parallel the discharged voltage was increased to ~ 0.48 V for the 2M-2C test, ~ 0.46 V for the 3M-2C test, and ~ 0.44 V for the 4M-2C test (Fig. 2). This steady decrease in boosted potential with the addition of MFCs showed that maintaining the same capacitance while charge is increased is detrimental to the circuits boosting capabilities. The voltage was not doubled (to 0.6 V) by this arrangement due to potential losses in the capacitor circuit, however, in all tests the voltage was boosted and remained stable at this boosted voltage during the entire batch. Through appropriately scaling the capacitance to meet the MFC charge capacity, the number of capacitors can be reduced while maintaining a boosted voltage which helps lessen the complexity of this combined system.

3.2. Hydrogen production rates

When two MFCs (2M) were connected in parallel directly to an MEC, the hydrogen production rate was $\sim 0.31 \text{ m}^3 \text{m}^{-3} \text{day}^{-1}$, and did not substantially increase when three or four MFCs were added (Fig. 3). However, the use of a two-capacitor circuit (2C, 0.02 F) increased hydrogen production rates by as much as 212%, with rates reaching $0.51 \text{ m}^3 \text{m}^{-3} \text{d}^{-1}$ (2M-2C), $0.72 \text{ m}^3 \text{m}^{-3} \text{d}^{-1}$ (3M-2C), and $0.80 \text{ m}^3 \text{m}^{-3} \text{d}^{-1}$ (4M-2C).

The use of three capacitors, and two MFC, resulted in a decreased hydrogen production rate. This reduction in performance was likely a result of the large capacitance relative to the limited current capability of the MFCs. If too many capacitors are

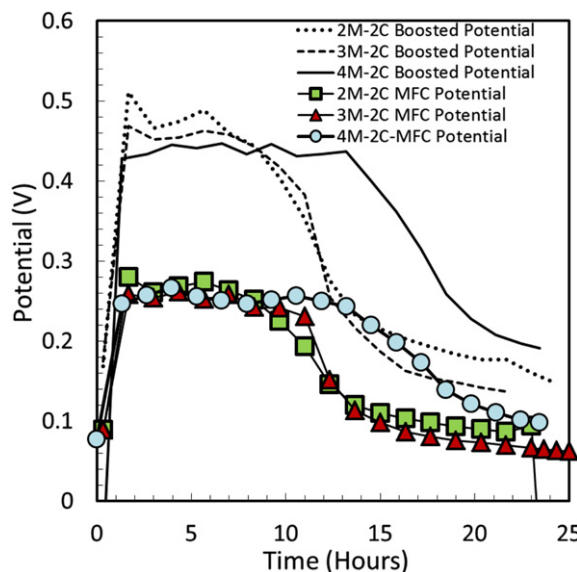


Fig. 2. Batch MFC and boosted potentials from tests with two capacitor circuits.

used in the circuit the capacitors will not fully charge, resulting in low voltages across each capacitor and low hydrogen production rates. With three MFCs and three capacitors (3M-3C), hydrogen production rates increased by 39% compared to three MFCs, but the production rate was 55% less than that produced using the 3M-2C circuit. The use of four MFCs (4M-3C) produced hydrogen gas at rates similar to that obtained using only two capacitors (4M-2C). There are clear trends visible between the hydrogen production rate and the number of capacitors used. As these systems are scaled, the trends observed between the number of MFCs and capacitance can be used to determine the appropriate capacitance needed to boost voltage and increase hydrogen production rates (Fig. 3). The optimal balance between the total capacitance, and the number of MFCs for these single chamber MFCs and MECs was found to be 0.01 F per 28 mL MFC. Using smaller than this ratio resulted in the capacitors filling to quickly and charge was lost due to a limited storage capacity. Larger ratios resulted in insufficient charge in each capacitor which translated to low voltages.

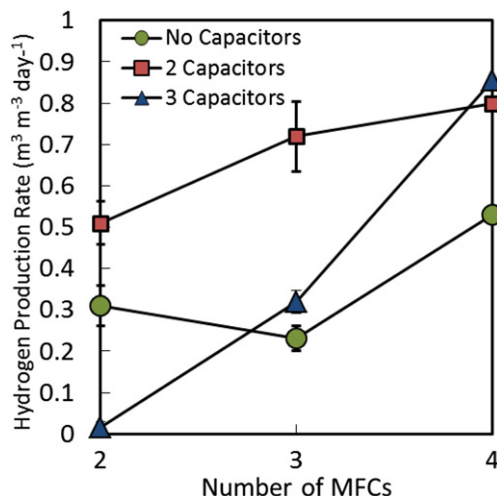


Fig. 3. Hydrogen production rates from varied numbers of MFCs and capacitors.

3.3. Coulombic efficiencies and hydrogen yields

Total system coulombic efficiencies (CE_{sys}) ranged from 30 to 60% (Fig. 4a). The CE for the MEC was consistently >90%, but the CE for the MFC was only 30–60%. When using the capacitor circuit, the CEs decreased by 45% (2M-2C), 16% (3M-2C) and 11% (4M-2C), compared to CEs obtained in tests without capacitors. The CE was reduced because the circuit has losses, and therefore it cannot transfer 100% of the charge produced by the MFC. As more MFCs (more charge) are introduced into the system the capacitors approach their maximum charge and the overall energy leakage is reduced, increasing the CE. In addition, as the number of MFCs was increased, the majority of the total substrate consumed by the MFCs was greater than that used in the MEC, making the overall CE governed by that of MFCs. Therefore the primary consequence with increasing the number of MFCs used to power the MEC is the increased substrate.

The total system hydrogen gas yield increased by a maximum of 50% with 3 MFCs (3M-2C), and by 11% with 4 MFCs (4M-3C) when using the capacitor-based circuit. The maximum MEC yield (3.1 mol H_2 mol-acetate⁻¹) and system hydrogen yields (0.4 mol H_2 mol-

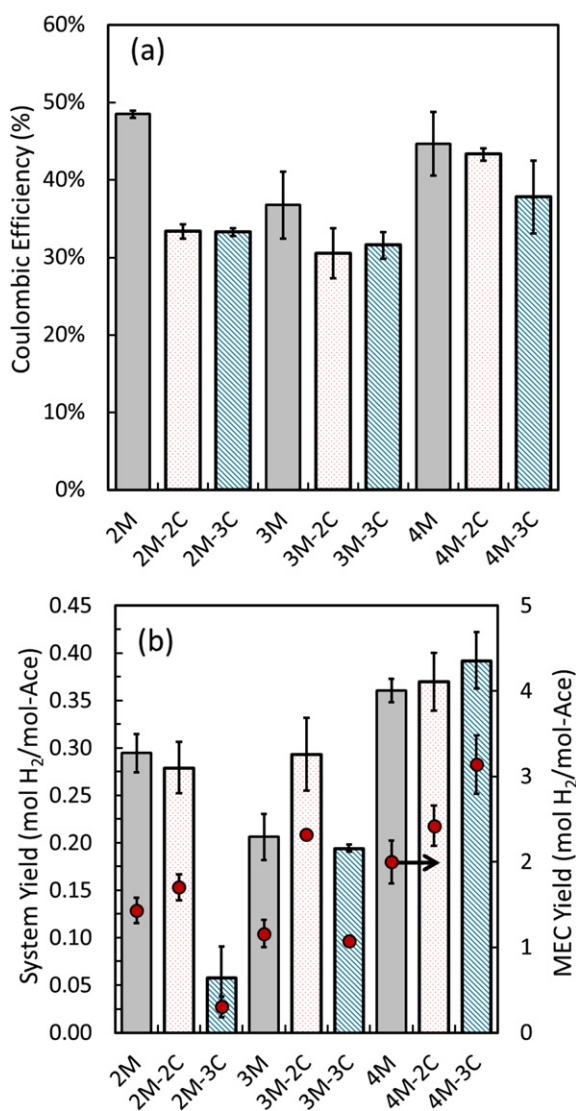


Fig. 4. (a) System Coulombic efficiencies, (b) System yield from substrate in both MFCs and the MEC, and MEC yield (moles H_2 /mole of substrate).

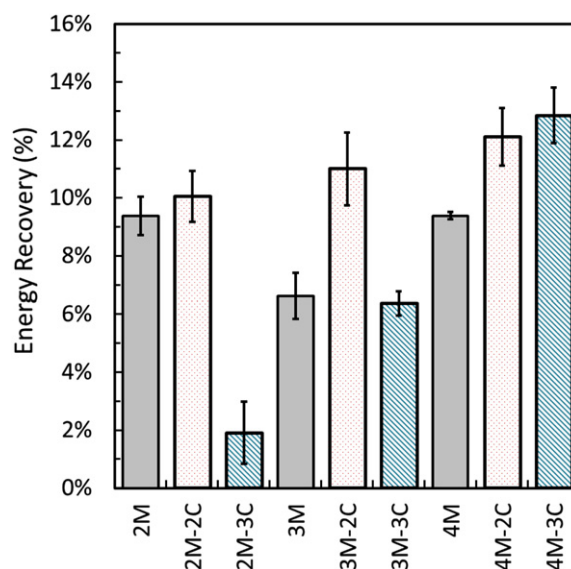


Fig. 5. Total energy recoveries from MFCs and the MEC.

acetate⁻¹) were achieved using the 3M-4C arrangement (Fig. 4b). This maximum MEC hydrogen gas yield is 60% greater than that previously achieved using MFCs connected in parallel to charge an MEC [8]. While the individual MEC yield was substantial, due to the large substrate concentrations (4 g L⁻¹) in the entire system (MFCs and MEC) as well as due to oxygen intrusion into the MFCs, the system yields were low. The air-cathode MFCs used here have low CEs due to aerobic degradation of substrate sustained by oxygen transfer through the cathode. The CEs could be increased by using MFCs that have separators between the electrodes, as these can reduce oxygen intrusion into the cube reactor [30].

3.4. Energy recovery

Overall energy recoveries were <10% using only MFCs (2M, 9.5%; 3M, 6.8%; 4M, 9.2%) (Fig. 5). The largest increase in energy

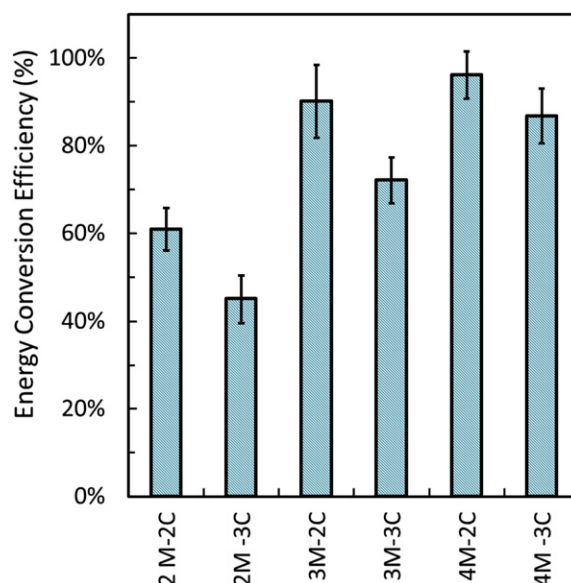


Fig. 6. Energy conversion efficiency from capacitor circuit.

recovery of 77% was obtained using the 3M-2C circuit, with smaller energy gains using other configurations (8%, 2M-2C; 30%, 4M-3C). The low energy recovery is mainly due to the energy recovery of the MFCs, which were all <7% [31]. The energy recovery of the MECs was very high, around 100%. Total energy recovery of the coupled MFC–MEC system might not be a primary concern, if the source of the organic matter is wastewater.

3.5. Electronic circuit efficiency

The capacitor circuit provided a simple and effective means of transferring upwards of 90% of the energy produced by the MFC to the MEC (Fig. 6). The maximum energy conversion efficiency of 95% was obtained using the 4M-2C configuration. As more charge (more MFCs) were used in the system, and the total capacitance was low, circuit energy efficiency increased. Previous energy storage circuits have only been shown to be capable of harvesting 43–75% [18] or 35.9% [17] of the energy produced by MFCs. Thus, significantly reduced performance would be achieved if these previous designs were directly connected to another system such as an MEC.

4. Conclusions

Adding capacitors to an MFC–MEC circuit increased system performance in terms of hydrogen production rates, energy recovery, and MEC yield, when the capacitance used was optimized to better align with the charge produced by the MFCs. For the single-chamber, air-cathode MFCs used here, the optimal capacitance per MFC was 0.01 F. With the addition of the capacitor circuit, the MFC–MEC system was shown to increase hydrogen production rates by 38%, MEC yields by 60% and energy recoveries by 77%. In addition, to maintain stability, all MFCs were aligned in parallel avoiding voltage reversal that occurs when MFCs are connected in series. Overall, the use of the capacitor circuit proved to be effective in storing and transferring up to 95% of the energy produced by the MFCs.

Acknowledgments

This research was supported by funding through the King Abdullah University of Science and Technology (KAUST) (Award KUS-I1-003-13), and by the National Science Foundation Graduate Research Fellowship Program.

References

- [1] H. Liu, S. Grot, B.E. Logan, *Environmental Science & Technology* 39 (2005) 4317–4320.
- [2] R.A. Rozendal, H.V.M. Hamelers, G.J.W. Euverink, S.J. Metz, C.J.N. Buisman, *International Journal of Hydrogen Energy* 31 (2006) 1632–1640.
- [3] D. Call, B.E. Logan, *Environmental Science & Technology* 42 (2008) 3401–3406.
- [4] J.Y. Nam, J.C. Tokash, B.E. Logan, *International Journal of Hydrogen Energy* 36 (2011) 10550–10556.
- [5] J.Y. Nam, R.D. Cusick, Y. Kim, B.E. Logan, *Environmental Science and Technology* 46 (2012) 5240–5246.
- [6] M. Mehanna, P.D. Kiely, D.F. Call, B.E. Logan, *Environmental Science & Technology* 44 (2010) 9578–9583.
- [7] M. Sun, G.-P. Sheng, L. Zhang, C.-R. Xia, Z.-X. Mu, X.-W. Liu, H.-L. Wang, H.-Q. Yu, R. Qi, T. Yu, M. Yang, *Environmental Science & Technology* 42 (2008) 8095–8100.
- [8] M. Sun, G.-P. Sheng, Z.-X. Mu, X.-W. Liu, Y.-Z. Chen, H.-L. Wang, H.-Q. Yu, *Journal of Power Sources* 191 (2009) 338–343.
- [9] A. Wang, D. Sun, G. Cao, H. Wang, N. Ren, W.-M. Wu, B.E. Logan, *Bioresource Technology* 102 (2011) 4137–4143.
- [10] H. Zhao, Y. Zhang, B. Zhao, Y. Chang, Z. Li, *Environmental Science & Technology* 46 (2012) 5198–5204.
- [11] Y. Zhang, I. Angelidaki, *Water Research* 46 (2012) 2727–2736.
- [12] B. Tartakovsky, M.F. Manuel, H. Wang, S.R. Guiot, *International Journal of Hydrogen Energy* 34 (2009) 672–677.
- [13] S.E. Oh, B.E. Logan, *Journal of Power Sources* 167 (2007) 11–17.
- [14] P. Aelterman, K. Rabaey, H.T. Pham, N. Boon, W. Verstraete, *Environmental Science & Technology* 40 (2006) 3388–3394.
- [15] C. Donovan, A. Dewan, H. Peng, D. Heo, H. Beyenal, *Journal of Power Sources* 196 (2011) 1171–1177.
- [16] A. Dewan, C. Donovan, D. Heo, H. Beyenal, *Journal of Power Sources* 195 (2010) 90–96.
- [17] H. Wang, J.D. Park, Z. Ren, *Environmental Science and Technology-Columbus* 46 (2012) 5247.
- [18] J.D. Park, Z. Ren, *Journal of Power Sources* 208 (2012) 322–327.
- [19] B. Zhang, Z. He, *RSC Advances* 2 (2012) 10673–10679.
- [20] Y. Kim, M.C. Hatzell, A.J. Hutchinson, B.E. Logan, *Energy & Environmental Science* 4 (2011) 4662–4667.
- [21] L. Woodward, M. Perrier, B. Srinivasan, R. Pinto, B. Tartakovsky, *AIChE Journal* 56 (2010) 2742–2750.
- [22] L. Woodward, B. Tartakovsky, M. Perrier, B. Srinivasan, *Biotechnology Progress* 25 (2009) 676–682.
- [23] L. Woodward, M. Perrier, B. Srinivasan, *Journal of Process Control* 19 (2009) 205–215.
- [24] R. Pinto, B. Srinivasan, S. Guiot, B. Tartakovsky, *Water Research* 45 (2011) 1571–1578.
- [25] W. Hill, *The Art of Electronics*, second ed., (1989). New York, NY.
- [26] H. Liu, B.E. Logan, *Environmental Science & Technology* 38 (2004) 4040–4046.
- [27] B. Logan, S. Cheng, V. Watson, G. Estadt, *Environmental Science & Technology* 41 (2007) 3341–3346.
- [28] S. Cheng, H. Liu, B.E. Logan, *Electrochemistry Communications* 8 (2006) 489–494.
- [29] S. Cheng, D. Xing, D.F. Call, B.E. Logan, *Environmental Science & Technology* 43 (2009) 3953–3958.
- [30] X. Zhang, S. Cheng, X. Wang, X. Huang, B.E. Logan, *Environmental Science & Technology* 43 (2009) 8456–8461.
- [31] H. Liu, S. Cheng, B.E. Logan, *Environmental Science & Technology* 39 (2004) 658–662.